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Calibration Standards for X-Ray Spectrometers Used for Pollution Sample Analysis

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CALIBRATION STANDARDS FOR X-RAY SPECTROMETERS
USED FOR POLLUTION SAMPLE ANALYSIS

by

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ABSTRACT

A technique is described for making aerosol standards for x-ray fluorescence analysis by depositing micron sized particles suspended in a carrier solution onto the surface of a Nuclepore filter. Size is controlled by a separate sedimentation step following grinding in a boron carbide mortar and pestle. Binding of the deposition to the filter uses a collodion film layer applied both before and after the particle deposition. The deposited mass is determined gravimetrically from a companion filter prepared from a large volume of carrier solution and without collodion. Standards for 24 different elements have been prepared.

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SECTION 1

INTRODUCTION

The need for reliable calibration standards is often not appreciated until considerable time and effort has been expended on instrument development. X-Ray standards are no different and each investigator has typically created his own special reference materials. This program to prepare x-ray standards has concentrated on the development of a technique which could be used with a variety of compounds to produce thin layers of finely divided particles on the surface of the supporting substrate so that particle size effects, interelement effects, and substrate absorption would be minimal. The final technique which has been adopted is deposition of previously sized particles from a suspension in isopropyl alcohol (IPA) onto a Nuclepore filter plus a collodion film binder. Other binder techniques have been attempted, in particular, softening of the Nuclepore filter, but these have proved unreliable in practice. Details of the final procedure are given in Section 3. A discussion of the evolution of the procedure is given in Section 4.

Information on the specific compounds used for the standards is collected within Section 5. This includes available information on purity, gravimetric data on mass depositions, and comments on the effects of particle size.

SECTION 2

RECOMMENDATIONS AND CONCLUSIONS

A successful deposition technique for the preparation of thin aerosol standards has been defined.

The essential steps include (1) grinding and sedimentation to control particle size to 1 micron and under, (2) suspension of particles in isopropyl alcohol, (3) filtration of a large volume of suspension to gravimetrically determine deposition rate, (4) deposition of a collodion film on the Nuclepore substrate prior to particle deposition, (5) particle deposition, and (6) deposition of a second collodion film to complete the binding. Essential details of the steps are described in other sections.

The problems encountered while developing the technique have been more severe than anticipated, however, and the final procedure itself is more complex and time consuming than the original estimates. Roughly, one should allow a man-week of effort for the production of 1 set of standards, i.e., a total of 6 filters of one element with 2 deposition diameters and 3 different thicknesses. Proficiency and development of parallel processing may eventually alter the time but experience has indicated that initially one third of the time will be spent on grinding, sedimentation, sizing, and calibration; one third of the time on dilution, deposition, and mounting of the 35 mm deposits; and one third of the time on dilution, deposition, and mounting of the 20 mm deposits. Any additional characterization such as microscopic measurements on size and uniformity requires additional time.

While grinding and suspension of each new compound presents a new situation and possible problems, the procedure is now relatively straightforward. Two areas for potential problems should be kept in mind, however. One is the filter holder design. We have found variations in manufacture of the supplied holders which cause wrinkling of the completed filter in the process of closing the holder. This can ruin a standard after the investment of considerable time and effort. The other area is compatibility with the isopropyl alcohol used for suspension. If a change in liquids is required, the deposition characteristics may be altered requiring a modification of the procedure.

SECTION 3

PROCEDURE FOR STANDARDS PREPARATION

The current procedure for producing calibration standards can best be described by dividing the entire process into four parts:

- A. Preparing the Suspension
- B. Filtering and Coating the Filters
- C. Mounting the Completed Filters in Permanent Retainers
- D. Packaging the Completed Filters

The advantages and disadvantages of the current procedure and its evaluation will be discussed in Section 4.

PREPARING THE SUSPENSION

Preparing suspensions involved essentially six (6) phases: (1) Microscopical examination of pure materials, (2) grinding, (3) weighing, (4) dispersal by sonification, (5) sedimentation, and (6) reweighing.

1. Powders are examined by optical microscopy to determine whether the particle size is suitable for immediate filtration or whether grinding is necessary.
2. When grinding is necessary, the powders are ground in a boron carbide mortar and pestle for approximately 20 minutes and then transferred to a clean vial.
3. One hundred milligrams (100 mg) of the ground sample is weighed on an analytical balance and transferred to a clean 150 ml beaker. Approximately 100 mls of IPA is added to the beaker.
4. The beaker containing the suspension is placed in an ultrasonic bath for 20 minutes to break up weakly bound agglomerates. The suspension is then cooled to room temperature and particles are allowed to settle for 20 minutes. This cycle is repeated 3 or 4 times to de-agglomerate the suspension as completely as possible.

5. The suspension is then allowed to settle for 20 minutes to remove the large particles. The fines are then carefully decanted into a 1000 ml volumetric flask and brought to volume with IPA. Most of the liquid is decanted leaving only the obvious sediment at the bottom.
6. The coarse fraction is then filtered through a pre-weighed Nuclepore membrane. After drying, the filter is reweighed. The difference in weight between the original 100 mg and the coarse fraction now on the filter gives the approximate weight of fines.

FILTERING THE SUSPENSIONS

Filtering suspensions involved (1) dilution, (2) filtration apparatus set-up, (3) filtration and coating, (4) drying, and (5) mass concentration determination. The first four steps are performed in a clean bench.

1. The approximate mass concentration of fines is used to estimate the suspension volume required to produce depositions in the desired range. Two different techniques were used to vary the mass being deposited. In Method I, the fines are first diluted to produce the suspension volume needed to produce the heaviest desired standard. The second most concentrated standard is then prepared by diluting the first suspension 1:10. The least concentrated standard is prepared from a 1:10 dilution of the second suspension. The suspensions then have a concentration ratio of 100:10:1. The same volume is used for each suspension to prepare the standards, thus insuring uniform precision. The Method I dilution technique was used during Phase 1 to prepare both the 20 mm and 30 mm standards, each size with 3 different concentrations (the 30 mm standard actually has a deposit over a 35 mm diameter). The 20 mm standards were made using half the volume of suspension used for the 30 mm standard. Subsequent doubts about the trace solubility of so-called "insoluble" compounds led to use of Method II which completely avoided multiple dilutions. Method II was used during the second phase of the program when 6 different deposits were prepared for each compound using a 35 mm diameter and no 20 mm standards were prepared. In Method II, the fines are diluted to produce the total suspension volume needed for all depositions with a concentration sufficiently dilute to permit use of at least 5 ml of suspension for the smallest deposit.
2. The filter support and funnel are thoroughly cleaned with IPA prior to filtration. The preparation of a 30 mm standard requires an 0.8 μ m Gelman membrane filter as an interface between the sintered metal support plant and the 0.4 μ m Nuclepore membrane which receives the particles. The Gelman filter produces a more uniform particle deposition. The two filters are rinsed in clean IPA and carefully positioned concentrically on the filter holder, Nuclepore on top, taking care that they are perfectly flat with no sign of wrinkling. This is achieved by

simultaneously wetting the filter with IPA and applying a slight vacuum to the mounted filter. The same procedure is used for the 20 mm standard but no interfacial filter is required.

3. With a slight vacuum applied, the Nuclepore membrane is sprayed with a nebulized mist of 5% commercial collodion in amyl acetate from a DeVilbiss Glass Nebulizer 40. The vacuum is gradually released and the filter funnel is carefully placed onto the mounted filter and clamped into place. Some IPA is added to the empty filter assembly and then gradually the suspension is rinsed thoroughly and completely into the assembly. A watch glass is placed over the funnel and vacuum is applied to the filter. During this stage of the process it is important to control the vacuum precisely, as too weak a vacuum will cause clogging of the filter and too strong a vacuum may cause non-uniform deposition, wrinkling or other problems. Occasionally, the cover glass is removed and the funnel wall gently rinsed with clean IPA to prevent sample loss, being careful not to disturb the suspension. When the filtrate is gone, revealing the substrate, the vacuum is made weaker, the clamp is removed and the upper funnel is carefully lifted off. The filter is checked visually under a magnifying glass for uniformity and boundary sharpness. Vacuum is again applied and the filter is sprayed with a nebulized mist of 0.1% solution of collodion in amyl acetate.
4. The vacuum is released and the filter is placed on a flat square of Teflon and left to dry under a large, clean glass cover.
5. The exact mass concentration of fines is determined by filtering a large volume of the most concentrated suspension through a pre-weighed Nuclepore membrane. The filter and residue are dried and reweighed to determine the precise weight of standard delivered to each filter standard.

MOUNTING THE COMPLETED FILTER

The filter holders supplied by the EPA (1) are comprised of two parts: (1) the lower portion onto which the finished filter is placed and (2) the upper retaining clip which holds the filter in place.

The completed filter is placed onto the bottom portion of the holder and edge only is wetted carefully with a 0.1% collodion solution avoiding the deposition entirely. The filter is then manipulated until it lies flat and virtually wrinkle free on the holder.

Next a small crescent of Nuclepore membrane, onto which is printed (in ink) the element name, concentration ratio and deposit area size, is placed along the filter's edge, serving as a label. The retaining clip is

compressed and placed over the filter and snapped into place in the bottom holder. This assembly is then permitted to dry under a watch glass in the clean hood.

PACKAGING OF COMPLETED FILTERS

Two clean 2" x 2" glass slides are assembled to form a sandwich into which the standard is placed, thus serving to protect the upper and lower surfaces of the filter.

DEPARTURES FROM STANDARD PROCEDURES

Certain compounds required special treatment. Such problems as solubility in IPA and distortion of the Nuclepore filter had to be overcome.

NaCl, SeO₂, As₂O₃ and KHCO₃ all proved to be soluble in IPA. This problem with NaCl was eliminated by preparing a suspension using a saturated solution of NaCl in water.

The use of other solvents such as acetone was precluded because it distorted the Nuclepore filter.

SECTION 4

DEVELOPMENT OF A PREPARATION TECHNIQUE

Initially a procedure for the preparation of the standards was attempted according to a different work plan. However, during the initial preparation of filters, several unexpected problems arose. These problems and our solutions to them are listed below.

PREPARATION OF SUSPENSIONS

Initially powders were selected on the basis of availability, purity, and particle size according to the suppliers' specifications. Under optical microscopy, however, it was determined that many more powders would require grinding than was previously anticipated. The pure metal powders particularly fell outside the claimed size range. Due to the difficulty of grinding metallic powders alternate sample selections were generally made.

To avoid contamination in the grinding process a boron-carbide mortar and pestle was used. These low atomic number elements give no interference for x-ray fluorescence studies.

FILTERING THE SUSPENSIONS

Dilution

Early attempts at filter preparation involved the use of volumetric pipettes rather than graduated cylinders. Pipettes seemed ideally suited to the situation since small amounts of suspension could be withdrawn accurately for the dilutions. However, upon further consideration it was realized that pipettes could not accurately nor economically be used for these dilutions.

Because only molecular "particle" sizes are encountered in a solution, pipettes can be used accurately to deliver small quantities. However, in a suspension, although mass concentration may be uniform, particle sizes are orders of magnitude larger and certain difficulties arise.

A pipette is designed specifically so that the delivered volume is correct when a small amount of liquid remains trapped in the bottom as implied by the designation TD (to deliver). This type pipette should not be blown out for accurate volume determination. Consequently, the pipette cannot be rinsed into the filtrate to remove particles adhering to the walls.

In order to avoid any cross contamination between suspensions, the pipette had to undergo a thorough cleaning process involving detergent rinsing, distilled water rinsing, acid bath and distilled water rinsing again. The preparation of six filters per standard set and one additional for mass determination rendering this method inaccurate and time consuming.

As an alternative, graduated cylinders were used with a small sacrifice in accuracy but with significant advantages due to ease in cleaning, thereby eliminating virtually all cross contamination in addition to the subsequent saving of time.

Filtration System Set-Up

The Delrin funnel shown in Figure 1 was used for both 35 mm and 20 mm standards (by inverting the funnel) when Method I was used to control mass deposition. The Delrin funnel in Figure 2 holds the larger volume required for the Method II procedure of controlling mass deposition.

As originally designed, the lower supports used specially fabricated screens to support the filter under vacuum. After several filters were prepared it was decided that they were unsatisfactory due to non-uniformity of deposition and indistinct outer boundary. It was our intention to produce a consistently uniform deposition with as sharp a boundary as possible. To this end several modifications were made. A sintered metal backing plate is used in the 35 mm support and the original support screen for the 20 mm screen was modified to accommodate the screen in a slightly recessed position.

In addition, for the 35 mm standard, it is necessary to use an 0.8 μ m Gelman filter underneath the Nuclepore membrane to assure a uniform filtration surface and prevent the deposit from assuming the surface features of the sintered metal backing plate. It took many attempts to finally find the corrected method for obtaining a uniform deposit.

Filtration and Coating

Ideally, our intention was to produce a high quality standard whose surface could be protected from dust and debris by a thin film which could withstand gentle brushing with a soft brush. However, due to the requirement for a very thin film, so as not to cause appreciable beam attenuation, problems arose as to choice of film and method of application. Altogether, four different methods of application were tried utilizing (1) collodion which is a film former, (2) polyvinylpyrrolidone (PVP) a film former, and (3) the combination of collodion and PVP. Comments on the use of these materials are as follows:

- (1) Collodion mixed directly into the filtrate for simultaneous deposition sometimes tended to clog the filter.
- (2) Collodion of PVP dropped gently onto the substrate after filtration destroyed the uniformity by forming spots.

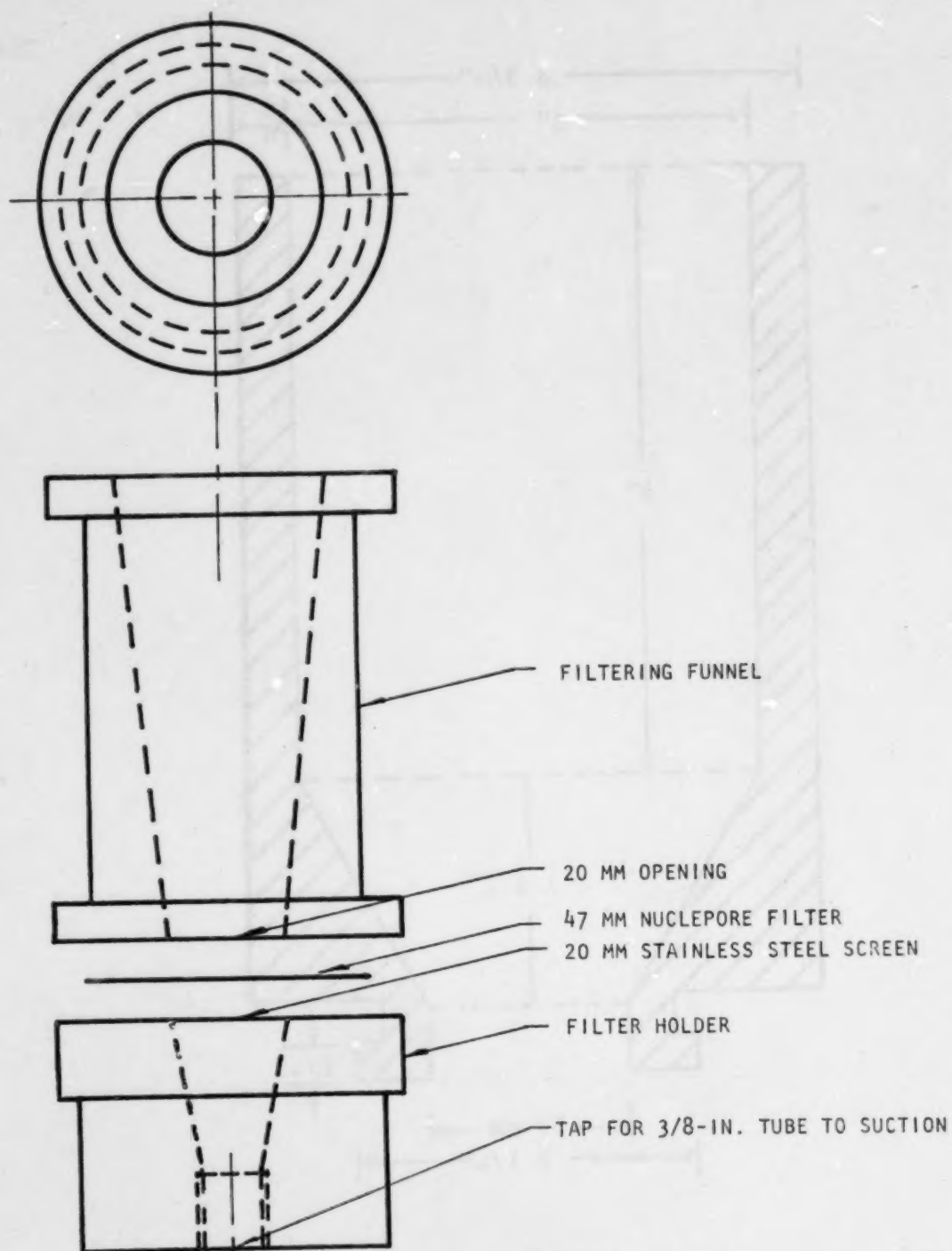


Figure 1. Filter apparatus for 20 mm and 35 mm deposits prepared during Phase 1

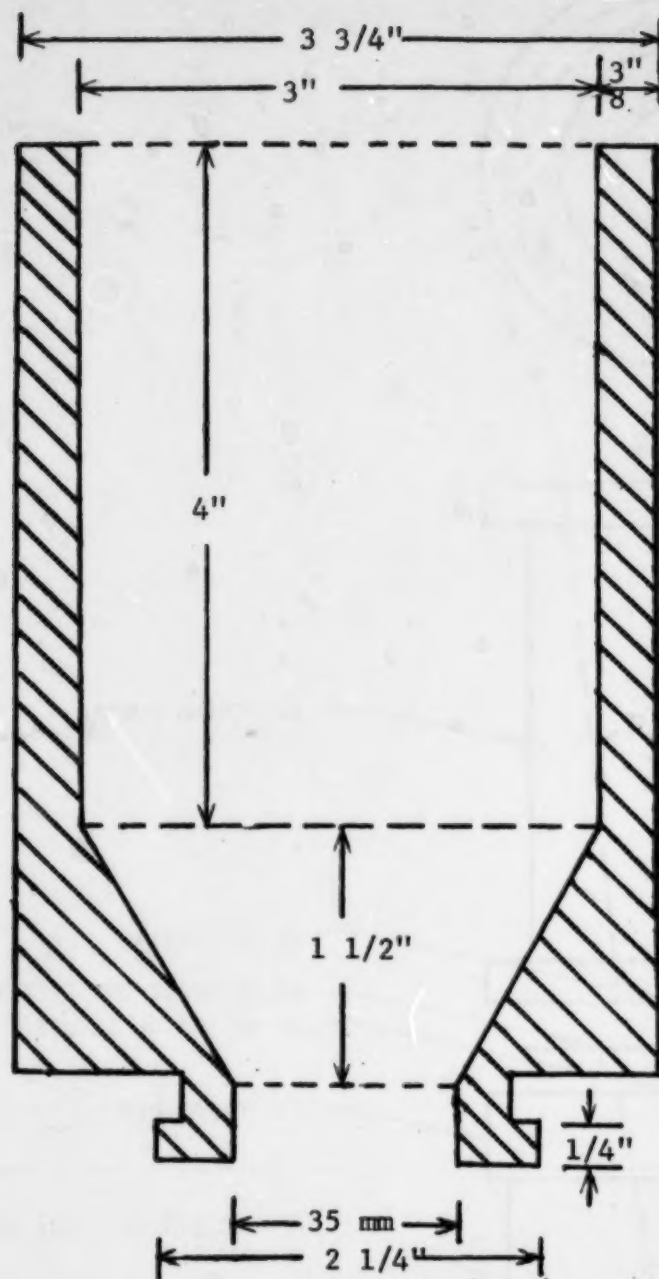


Figure 2. Filter apparatus for 35 mm deposits prepared during Phase 2

An approximate calculation also showed the film to be too thick.

- (3) Collodion sprayed on the substrate only after filtration was an improvement but did not provide adequate protection.
- (4) The technique eventually selected involves a collodion spray before and after the deposition and was described in Section 3.

The theory behind this technique is that the first spraying with 5% collodion solution deposits a thin film of collodion on the filter onto which the particles will rest. The 0.1% collodion spray serves primarily to wet the particles and bind them to the heavier collodion layer below the particles.

The concentration of the first collodion spray is not crucial but it cannot be so great as to clog the filter. On the other hand the second spray concentration is important since it must meet the criterion of minimum x-ray attenuation. Experimentation and rough calculation showed that our use of a 0.1% collodion solution could not deposit more than a few hundredths of a micron thick film. Since a thickness of 0.1 μm was acceptable, the film thickness deposited was well within tolerable limits.

Mass Concentration

Mass concentration of fines was initially obtained using a Cahn Electro-balance. The only problem has been the charging of the Nuclepore filters which makes accurate weighing difficult. This persistent problem with microbalance measurements was partially overcome using a Polonium-210 radiation source to discharge the membrane. However, this has not been entirely successful and great care is required to make a good measurement. The final procedure adopted is to filter a large volume of suspension and weigh the residue on a semi-micro balance (± 0.05 mg sensitivity). See Section 5 for further details.

Mounting the Completed Filter

During the process of mounting the filters, there is a tendency for them to wrinkle. This occurs because the upper retaining clip exerts stresses on the filter and bottom holder which don't exist before the clip is inserted. Apparently this difficulty cannot be surmounted with the filter holders presently in use.

Packaging the Completed Filter

There is no problem associated with packaging the standards.

SECTION 5

COMPLETED STANDARDS

A total of 24 standards have been prepared. These compounds are Cr_2O_3 , MnO_2 , RhO_2 , Fe_2O_3 , V_2O_5 , Sb_2O_3 , CaF_2 , Al_2O_3 , As_2O_3 , TiO_2 , CuO , NiO , BaSO_4 , Co_3O_4 , PtO , ZnO , PdO , SnO_2 , Ag , SiO_2 , MoO_3 , HgO , WO_3 and NaCl . The calibration of these standards is purely gravimetric as described in the next section.

CHARACTERIZATION OF COMPLETED STANDARDS

Mass

The correlation between deposited mass and volume of the suspension is first determined by filtering and weighing a large (approximately 1000 ml) volume and weighing the resulting deposit. This correlation is used for both size standards since the same stock suspension is used throughout. Table 1 gives the gross and tare weights determined from multiple measurements of the calibration deposit.

The volume of stock solution used for the heaviest deposit is tabulated in Table 2 along with the resulting compound and elemental mass per unit area. The larger deposition diameter is 35 mm. The surface density for the 20 mm deposit can be obtained from the 35 mm deposit with allowance for the reduced area and the fact that only half as much solution is used for the 20 mm deposits.

Based on the deposits in Table 2, the reported mass values for the filters of each size are given in Table 3.

The largest source of error is introduced by the dilutions and this depends on the size of the graduate used and the number of dilutions. The maximum error in a 35 mm deposit would be for MnO_2 for which a 5 ml cylinder was used for 3 measurements. This introduces, in conjunction with 2 measurements of 50 ml, an uncertainty of about 3.6% for the maximum dilution. Dilution errors for other cases will be less.

Chemical Purity

Table 4 summarizes the available data on the chemical compounds used for the standards.

Table 1. CALIBRATION DATA FOR STOCK SUSPENSION

<u>Compound</u>	<u>Gross Weight</u>	<u>Tare Weight</u>	<u>Net Deposit, g</u>	<u>Volume Filtered, ml</u>
<u>Group A</u>				
CaF ₂	.02211	.01423	.00788	1000
Al ₂ O ₃	.01756	.01418	.00338	1000
SiO ₂	.01524	.01343	.00181	500
As ₂ O ₃	.01438	.01264	.00174	1000
TiO ₂	.01600	.01409	.00191	1000
CuO	.01478	.01385	.00093	1000
NiO	.01598	.01422	.00176	1000
BaSO ₄	.01868	.01453	.00415	1000
Co ₃ O ₄	.01485	.01386	.00099	500
PtO ₂	.01835	.01466	.00369	1000
ZnO	.01675	.01413	.00262	1000
MoO ₃	.01723	.01416	.00307	1000
<u>Group B</u>				
PdO	.01694	.01421	.00273	500
SnO ₂	.01622	.01421	.00201	1000
Ag	.02442	.01386	.01056	1000
HgO	.01604	.01428	.00176	1000
WO ₃	.01790	.01464	.00326	1000
NaCl	.01937	.01394	.00543	1000
Cr ₂ O ₃	.05797	.01362	.04434	500
MnO ₂	.03804	.01378	.02426	500
RhO ₂	.05011	.01401	.03610	400

Table 1 (cont.)

<u>Compound</u>	<u>Gross Weight</u>	<u>Tare Weight</u>	<u>Net Deposit, g</u>	<u>Volume Filtered, ml</u>
Fe_2O_3	.02485	.01515	.00970	100
V_2O_5	.01778	.01508	.00270	500
Sb_2O_3	.02333	.01400	.00933	500

Table 2. SURFACE DENSITY CALCULATION FOR HEAVIEST 35 MM STANDARD

Compound	Suspension Concentration, mg/ml	Volume Used for Heaviest 35 mm Deposit, (ml)	Mass Delivered to Heaviest 35 mm Deposit, μg	Compound Density $\mu\text{g}/\text{cm}^2$	Gravimetric Factor	Elemental Density, $\mu\text{g}/\text{cm}^2$
Group A						
CaF_2	0.00788	500	3,940	409	0.513 (Ca) 0.486 (F)	210 199
Al_2O_3	0.00338	500	1,690	176	0.529	92.9
SiO_2	0.00362	500	1,810	188.1	0.467	87.9
As_2O_3	0.00174	500	870	90.4	0.757	68.5
TiO_2	0.00151	500	955	99.3	0.600	59.6
CuO	0.00093	500	465	48.3	0.799	38.6
NiO	0.00176	500	880	91.5	0.786	71.9
BaSO_4	0.00415	500	2,075	215.7	0.588 (Ba)	126.8
Co_3O_4	0.00198	500	990	102.9	0.734	75.5
PtO_2	0.00369	500	1,845	191.8	0.859	165
ZnO	0.00262	500	1,310	136	0.803	109
MoO_3	0.00307	500	1,535	159.6	0.667	106
Group B						
PdO	0.00546	500	2,730	283.8	0.870	247
SnO_2	0.00201	500	1,005	104	0.788	82.3
Ag	0.01056	500	5,280	549	1	549
HgO	0.00176	500	880	91.5	0.926	84.7
WO_3	0.00326	500	1,630	169	0.793	134
NaCl	0.00543	500	2,715	282	0.393 (Na) 0.607 (Cl)	111 171
Cr_2O_3	0.08868	10	886.8	92.2	0.684	63.1
MnO_2	0.04851	5	242.6	25.2	0.632	15.9

Table 2 (cont.)

Compound	Suspension Concentration, mg/ml	Volume Used for Heaviest 35 mm Deposit, (ml)	Mass Delivered to Heaviest 35 mm Deposit, μg	Compound Density $\mu\text{g}/\text{cm}^2$	Gravimetric Factor	Elemental Density, $\mu\text{g}/\text{cm}^2$
RhO_2	0.09024	10	902.4	93.8	0.763	71.6
Fe_2O_3	0.09698	10	969.8	100.8	0.699	70.5
V_2O_5	0.00540	10	54.0	5.61	0.555	3.12
Sb_2O_3	0.01866	20	373.2	38.8	0.835	32.4

Table 3. ELEMENTAL DEPOSITS ON THE SUPPLIED AEROSOL STANDARDS

Compound	Elemental Mass on the 35 mm Deposits, $\mu\text{g}/\text{cm}^2$
CaF_2 (Ca)	210 , 105 , 21.0 , 10.5 , 4.20 , 2.10
(F)	199 , 99.5, 19.9 , 9.95, 3.98 , 1.99
Al_2O_3	92.9, 46.5, 9.29, 4.65, 1.86 , 0.929
SiO_2	87.9, 43.9, 8.79, 4.39, 1.76 , 0.879
As_2O_3	68.5, 34.2, 6.85, 3.42, 1.37 , 0.685
TiO_2	59.6, 29.8, 5.96, 2.98, 1.19 , 0.596
CuO	38.6, 19.3, 3.86, 1.93, 0.772, 0.386
NiO	71.9, 35.9, 7.19, 3.59, 1.44 , 0.719
BaSO_4 (Ba)	127 , 63.4, 12.7 , 6.34, 2.54 , 1.27
Co_3O_4	75.5, 37.8, 7.55, 3.78, 1.51 , 0.755
PtO_2	165 , 82.4, 16.5 , 8.24, 3.29 , 1.65
ZnO	109 , 54.7, 10.9 , 5.47, 2.19 , 1.09
MoO_3	106 , 53.2, 10.6 , 5.32, 2.13 , 1.06
<u>Group B</u>	
PdO	247 , 123 , 24.7 , 12.3 , 4.94 , 2.47
SnO_2	82.3, 41.2, 8.23, 4.12, 1.65 , 0.823
Ag	549 , 274 , 54.9 , 27.4 , 11.0 , 5.49
HgO	84.7, 42.3, 8.47, 4.23, 1.69 , 0.847
WO_3	134 , 67.2, 13.4 , 6.72, 2.69 , 1.34
NaCl (Na)	111 , 55.5, 11.1 , 5.55, 2.22 , 1.11
(Cl)	171 , 85.6, 17.1 , 8.56, 3.43 , 1.71

Table 3 (Cont'd)

Compound	Elemental Mass Density ² on the 35 mm Deposits, g/cm	Elemental Mass Density ² on the 20 mm Deposits, g/cm
Cr_2O_3	63.1 , 6.31 , 0.631,	96.6 , 9.66 , 0.966
MnO_2	15.9 , 1.59 , 0.159,	24.4 , 2.44 , 0.244
RhO_2	71.6 , 7.16 , 0.716,	109.6 , 10.96 , 1.096
Fe_2O_3	70.5 , 7.05 , 0.705,	107.9 , 10.79 , 1.079
V_2O_5	3.12, 0.312, 0.312,	4.77, 0.477, 0.0477
Sb_2O_3	32.4 , 3.24 , 0.324,	49.6 , 4.96 , .496

Table 4. ANALYSIS DATA FOR COMPOUNDS USED IN DELIVERED STANDARDS

Compound	Supplier	Lot No.	Analysis Data
CaF ₂	Spex		99.999%
Al ₂ O ₃	Johnson-Matthay (JMC) 345	S.52652E	Si 3 ppm Ca 2 Fe 2 Mg 1 Cr <1 Cu <1
SiO ₂	JMC 425	S.53797	Ca 3 ppm Fe 2 Mg <1 Ag <1
As ₂ O ₃	JMC 642	S.52136C	Sb 6 Si 2 Fe 1 Cu <1 Mg <1
TiO ₂	JMC 435	S.52138B	Si 5 Na 2 Mg <1
CuO	JMC 40	S.52378A	Bi 6 Si 1 B <1 Cd <1 Ca <1 Fe <1 Mg <1 Ag <1
NiO	JMC 895	S.53375/b	Al 3 Bi 3 Si 3 Ca <1 Cr <1 Cu <1 Fe <1 Mg <1
BaSO ₄	Spex	10741	Ba 57.5% Mg 1-5 ppm Si 1-5 Ca 0.5-2 Na 0.5-2 Fe 0.5-2

Table 4 (cont.)

Compound	Supplier	Lot No.	Analysis Data
Co_3O_4	JMC 875	S.50951D 1	Si 7 ppm Ni 5 Fe 2 Al <1 Ca <1 Cu <1 Mg <1 Ag <1
PtO_2	Research Organic/Inorganic		99.9%
ZnO	JMC 155	S.52971B	Fe 3 ppm Cd 2 Mg 2 Si 1 Ca <1 Cu <1 Mn <1 Na <1
MoO_3	JMC	S.52534	Mg 5 ppm Cu 3 Fe 3 Ca <1 Si <1
PdO	Spex	11741	Fe 5-20 ppm Sn 5-20 Pd 87.9% Pt 10-30 ppm Si 10-30 Bi 5-20 Pb 5-20 Mg 5-20
SnO_2	JMC	S 53523C C	Si 10 ppm Ca 3 Al 1 Mg <1 Na <1
HgO	JMC 191	S 53625	Si 7 Cr 2 Cd 1 Cu <1 Mg <1 Ag <1

Table 4 (cont.)

Compound	Supplier	Lot No.	Analysis Data
Ag	Aremco Prod.		99.9%
WO ₃	JMC	S.54434D	Mo 1 Mg <1
Sb ₂ O ₃	Spex	07741	Sb 82.2% Si 2-5 ppm Mg 0.5-1 ppm Cu 0.5-1 Fe 0.5-1 Bi 0.5-1
Cr ₂ O ₃	JMC 705	S.51597F	Si 4 ppm Na 3 Cu <1 Mg <1
Fe ₂ O ₃	Pfizer	R3098R Lot 55	Fe ₂ O ₃ 99.5% SiO ₂ 200 ppm CaO 110 MgO 50 Na 50 Zn 70 Mn 660 Pb 12 As <1 Hg <0.1 Water soluble salts 0.04%
MnO ₂	JMC 815	S.51800A	Si 5 ppm Mg 2 Ca 1 Cu 1
RhO ₂	Spex	10691	Ni 50-100 ppm Pt 5-20 Pd 5-20 Fe 1-5 Mg 1-5 Cu 1-5 Pb 1-5 Ru 5-20

Table 4 (cont.)

Compound	Supplier	Lot No.	Analysis Data
V_2O_5	JMC	S534598	Al 1 ppm Ca <1 Cu <1 Fe <1 Mg <1 Si <1

Size and Uniformity

Visual inspection of the completed standards by optical microscopy indicated most particles were 1 micron or under in size. An occasional larger particle, probably an agglomeration of smaller particles, up to 10 micron can be seen. The particle distribution presents a visually uniform appearance.

Initially, an analysis of size and uniformity was planned using an electronic image analyzer. The confused image created by the numerous pores in the Nuclepore filter, however, has prevented using this quick but quantitative technique. Data from visual microscopy are given in Table 5.

X-Ray Characterization

The x-ray absorption characteristics for all the compounds of interest are given in Table 6. This includes the absorption coefficient and the mean free path for the fluorescent x-rays in the specified compound. Most of the data are for the K lines but data for L and M lines is included if these are likely to be used.

Particle Size Effects

In thin deposits such as these standards, allowance for the effect of particle size on response depends on the x-ray absorption characteristics, i.e., self-shielding properties, of the particles. For a complete description of the effect, the energy distribution of both the incident and emitted x-rays as well as the typical geometry of the particle must be well specified. In practice, the particle geometry is often poorly or only approximately determined.

If information on the approximate particle size is available, one can estimate the expected effects using formulas such as reviewed in Reference (2).

Alternatively, one can determine the effective particle size by making two separate fluorescence measurements on each sample using two different energies of excitation radiation (3). Since the sample mass is the same in both cases, any observed difference in response can generally be ascribed to particle size effects. Corrections for the effect can then be made.

A first order estimate of the significance of particle size or self shielding effects can be made by comparing the particle diameter with the radiation mean free path. A large ratio of diameter to mean free path obviously implies significant self absorption within the sample.

The approximate losses can be put on a quantitative basis by calculating the fraction of x-rays escaping from a spherical particle, (radius = R), with x-rays generated uniformly throughout the volume. This assumes

Table 5. PARTICLE SIZE DATA FOR LIGHT ELEMENTS

Compound	Size Range	Number of Particles	Number Percent
CaF ₂	<2 μ m	185	35.6%
	2-5	293	56.3
	5-10	39	7.5
	>10	3	0.6
		520	100.0%
BaSO ₄	<2 μ m	37	9.2%
	2-5	291	72.8
	5-10	69	17.2
	>10	3	0.8
		400	100.0%
MoO ₃	<2 μ m	177	42.5%
	2-5	227	54.6
	5-10	10	2.4
	>10	2	.5
		416	100.0%
NaCl	<5.3 μ m	71	14.1%
	5.3-15.9	146	29.0
	15.9-26.5	135	26.8
	26.5-53	120	23.9
	>53	31	6.2
		503	100.0%
Al ₂ O ₃	<5.3 μ m	238	55.0%
	5.3-10.6	156	36.0
	10.6-21.2	33	7.6
	>21.2	6	1.4
		433	100.0%

X-RAY CHARACTERISTICS FOR ELEMENTS AND COMPOUNDS OF INTEREST
(E = X-Ray Energy, μ = Mass Absorption Coefficient, and λ = X-Ray Mean Free Path)

Element	Compound	Density gm/cm ³	Line	E keV	μ cm ² /gm	λ Micron	Line	E keV	μ cm ² /gm	λ Micron	Line	E keV	μ cm ² /gm	λ Micron
Al	Al	2.702	Al K α	1.487	385.7	9.60	-	-	-	-	-	-	-	-
	Al ₂ O ₃	3.965	Al K α	1.487	912.1	2.77	-	-	-	-	-	-	-	-
Sb	Sb ₂ O ₃	5.2	-	-	-	-	Sb L α 1	3.605	365.6	5.26	-	-	-	-
As	As ₂ O ₃	3.738	As K α	10.53	30.1	88.9	As L α 1	1.282	1737.6	1.54	-	-	-	-
Ba	BaCO ₃	4.43	-	-	-	-	Ba L α 1	4.465	239.5	9.43	-	-	-	-
	BaSO ₄	4.50	-	-	-	-	Ba L α 1	4.465	265.3	8.38	-	-	-	-
Br	PbBr ₂	6.66	Br K α	11.91	62.0	24.2	Br L α 1	1.480	2103.6	0.714	-	-	-	-
	NaBr	3.203	Br K α	11.91	27.2	114.8	Br L α 1	1.480	1759.4	1.77	-	-	-	-
	RbBr	3.35	Br K α	11.91	35.0	85.3	Br L α 1	1.480	1413.8	2.11	-	-	-	-
Ca	CaCO ₃	2.710	Ca K α	3.691	116.4	31.7	-	-	-	-	-	-	-	-
	Ca(OH) ₂	2.24	Ca K α	3.691	125.4	35.6	-	-	-	-	-	-	-	-
Cd	CdO	6.95	-	-	-	-	Cd L α 1	3.133	453.0	3.18	-	-	-	-
Cl	LiCl	2.068	Cl K α	2.622	175.1	27.6	-	-	-	-	-	-	-	-
Cr	Cr	7.20	Cr K α	5.412	88.2	15.7	-	-	-	-	-	-	-	-
	Cr ₂ O ₃	5.21	Cr K α	5.412	72.8	26.4	-	-	-	-	-	-	-	-
Co	Co	8.9	Co K α	6.926	64.9	17.3	-	-	-	-	-	-	-	-
	Co ₃ O ₄	6.07	Co K α	6.926	52.8	31.2	-	-	-	-	-	-	-	-
Cu	Cu	8.92	Cu K α	8.040	53.7	20.9	-	-	-	-	-	-	-	-
	CuO	6.4	Cu K α	8.040	45.5	34.3	-	-	-	-	-	-	-	-
Au	Au ₂ O ₃	*	-	-	-	-	Au L α 1	9.712	114.4	*	Au M α	2.12	1069.1	*
F	LiF	2.635	F K α	0.679	832.2	4.56	-	-	-	-	-	-	-	-
Fe	Fe	7.86	Fe K α	6.401	71.4	17.8	-	-	-	-	-	-	-	-
	Fe ₂ O ₃	5.24	Fe K α	6.401	57.3	33.3	-	-	-	-	-	-	-	-
Pb	Pb	11.34	-	-	-	-	Pb L α 1	10.55	116.6	7.56	Pb M α	2.342	983.0	.897
	PbO ₂	9.375	-	-	-	-	Pb L α 1	10.55	98.5	10.83	Pb M α	2.342	890.0	1.20
	Pb ₃ O ₄	9.1	-	-	-	-	Pb L α 1	10.55	106.3	10.3	Pb M α	2.342	930.2	1.18
Hg	Hg	1.74	Hg K α	1.254	463.6	12.4	-	-	-	-	-	-	-	-
	HgF ₂	*	Hg K α	1.254	2051.1	*	-	-	-	-	-	-	-	-
	HgO	3.58	Hg K α	1.254	1245.4	2.24	-	-	-	-	-	-	-	-
Mn	MnO ₂	5.026	Mn K α	5.895	61.6	32.3	-	-	-	-	-	-	-	-
	MnCO ₃	3.125	Mn K α	5.895	52.1	61.4	-	-	-	-	-	-	-	-

Table 6 (cont.)

Element	Compound	Density gm/cm ³	Line	E keV	μ cm ² /gm	λ Micron	Line	E keV	μ cm ² /gm	λ Micron	Line	E keV	μ cm ² /gm	λ Micron
Hg	HgO	11.1	-	-	-	-	Hg L α 1	9.987	115.1	7.83	Hg M α	2.195	1043.2	
Mo	Mo	10.2	Mo K α	17.46	19.1	51.3	Mo L α 1	2.293	728	1.35	-	-	-	
	MoO ₃	4.692	Mo K α	17.46	13.2	161.5	Mo L α 1	2.293	633.1	3.37	-	-	-	
	MoS ₂	4.80	Mo K α	17.46	15.65	133.1	Mo L α 1	2.293	533.7	3.90	-	-	-	
Ni	Ni	8.90	Ni K α	7.473	58.9	19.1	-	-	-	-	-	-	-	
	NiO	6.67	Ni K α	7.473	49.7	30.2	-	-	-	-	-	-	-	
Pd	PdO	8.70	-	-	-	-	Pd L α 1	2.838	514.9	2.23	-	-	-	
P	P ₃ N ₅	*	P K α	2.014	322.2	*	-	-	-	-	-	-	-	
Pt	PtO ₂	10.2	-	-	-	-	Pt L α 1	9.441	114.4	8.57	Pt M α	2.048	1109.6	0.884
K	KHCO ₃	2.17	K K α	3.313	143.9	32.0	-	-	-	-	-	-	-	
	KNO ₃	2.109	K K α	3.313	148.5	31.9	-	-	-	-	-	-	-	
Rh	RhO ₂	*	-	-	-	-	Rh L α 1	2.696	519.1	*	-	-	-	
Se	SeO ₂	3.95	Se K α	11.21	26.2	96.6	Se L α 1	1.379	1543.4	1.64	-	-	-	
Si	SiO ₂	2.65	Si K α	1.740	667.8	5.65	-	-	-	-	-	-	-	
Ag	Ag	10.5	-	-	-	-	Ag L α 1	2.984	521.9	1.82	-	-	-	
	Ag ₂ O	7.143	-	-	-	-	Ag L α 1	2.984	500.4	2.80	-	-	-	
Na	Na ₂ SO ₄	2.68	Na K α	1.041	2565.8	1.45	-	-	-	-	-	-	-	
	Na ₂ CO ₃	2.532	Na K α	1.041	2349.6	1.68	-	-	-	-	-	-	-	
S	S	1.92	S K α	2.307	239.4	21.8	-	-	-	-	-	-	-	
	(NH ₄) ₂ SO ₄	1.769	S K α	2.307	323.6	17.5	-	-	-	-	-	-	-	
Sn	Sn	7.28	-	-	-	-	Sn L α 1	3.443	437.4	3.14	-	-	-	
	SnO ₂	6.95	-	-	-	-	Sn L α 1	3.443	374.5	3.84	-	-	-	
Tl	TlO ₂	4.26	Tl K α	4.512	92.6	25.4	-	-	-	-	-	-	-	
W	W	19.35	-	-	-	-	W L α 1	8.396	150.8	3.43	W M α	1.774	1465.6	0.353
	WO ₃	7.16	-	-	-	-	W L α 1	8.396	121.9	11.5	W M α	1.774	1351.0	1.03
U	U ₃ O ₈	8.3	-	-	-	-	U L α 1	13.612	80.7	14.9	U M α	3.165	615.0	1.96
V	V ₂ O ₅	3.357	V K α	4.951	77.3	38.5	-	-	-	-	-	-	-	
Zn	Zn	7.14	Zn K α	8.631	49.0	28.6	-	-	-	-	-	-	-	
	ZnO	5.606	Zn K α	8.631	41.4	43.1	-	-	-	-	-	-	-	

negligible attenuation of the stimulating radiation within individual particles. The fraction, f , of x-rays which escape in any given direction is given by (see Appendix):

$$f = \frac{3}{(\Sigma R)^2} - \frac{3}{2(\Sigma R)^3} (1 - e^{-2\Sigma R})(1 + \Sigma R)$$

where Σ is the macroscopic x-ray absorption cross section ($= 1/\text{mean-free-path}$). Figure 3 is a plot of f versus the size parameter D/λ , where D = diameter and λ = mean free path.

An alternative way to plot the same equation is given in Figure 4. Explicit values of the mean free path, λ , such as given for the calibration standards, can be used to enter the graph. The emission rate for different size spherical particles can then be read out directly.

Generally, if the emission is to be greater than 90% for 1 micron particles, then the mean free path should be greater than 4.7 micron.

The tabulated values for the mean free path in the standards provided indicate that they are all greater than 5 micron except for Al_2O_3 , PbO , SnO_2 , Ag and MoO_3 . Losses should therefore be less than 10% for the deposits since they are generally under 1 micron in size.

MATERIALS SELECTION AND TARGET VALUES

Catalogs from about 100 chemical supply houses were examined to determine sources of material. The initial list of possible compounds was based on chemical simplicity, purity available, particle size, certification, etc. A second list of simple compounds which are likely to be present in aerosol samples was also prepared as a useful alternative compound. The initial screening of these lists produced a list which contained generally acceptable compounds. Table 7 contains the list of chemical forms finally selected for deposition.

The formula weights, gravimetric factors, and desired surface density for each of these compounds is given in Tables 8 and 9.

*Density not available.

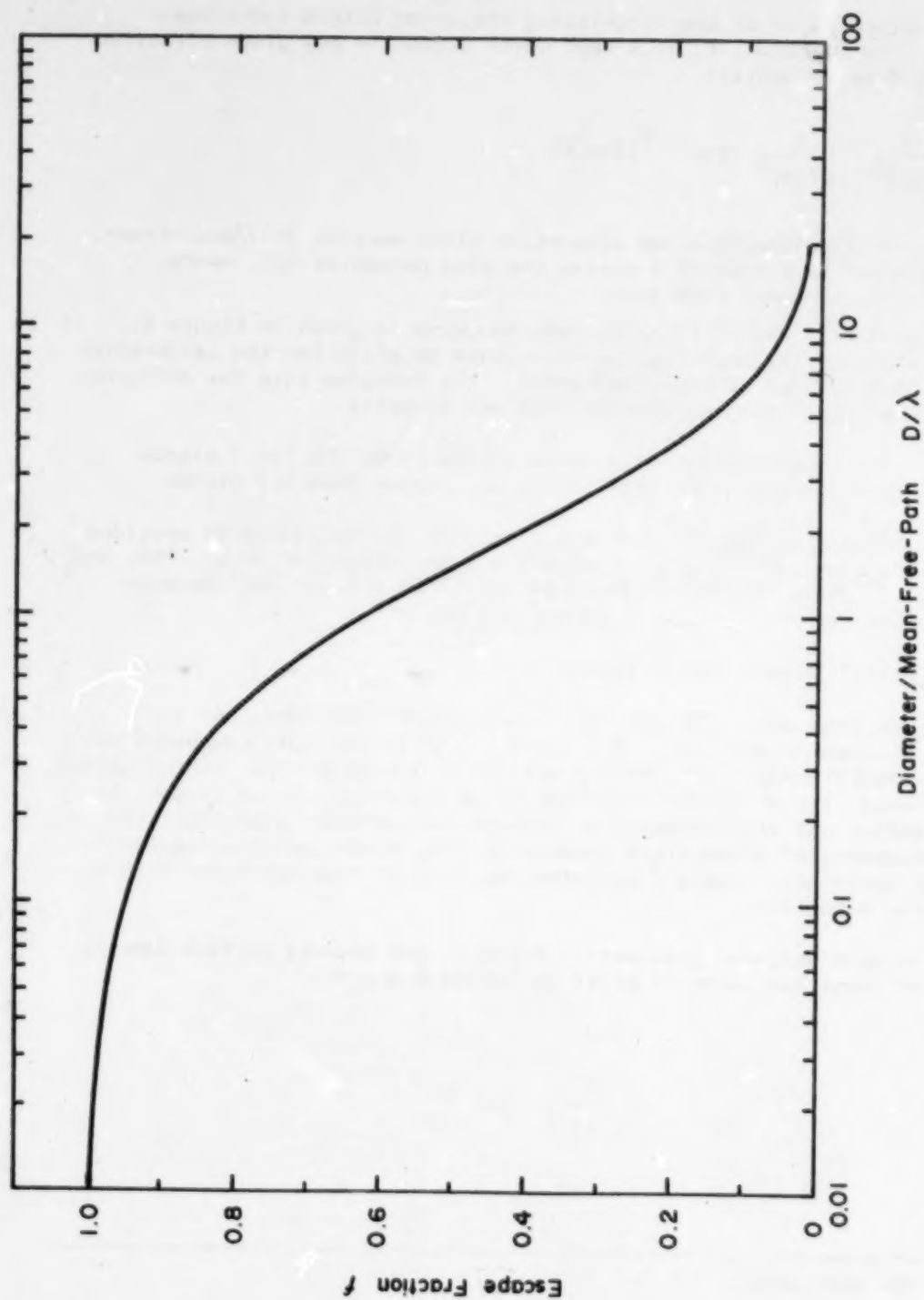


Figure 3. Probability of escape from a uniform spherical source as a function of diameter/mean-free path

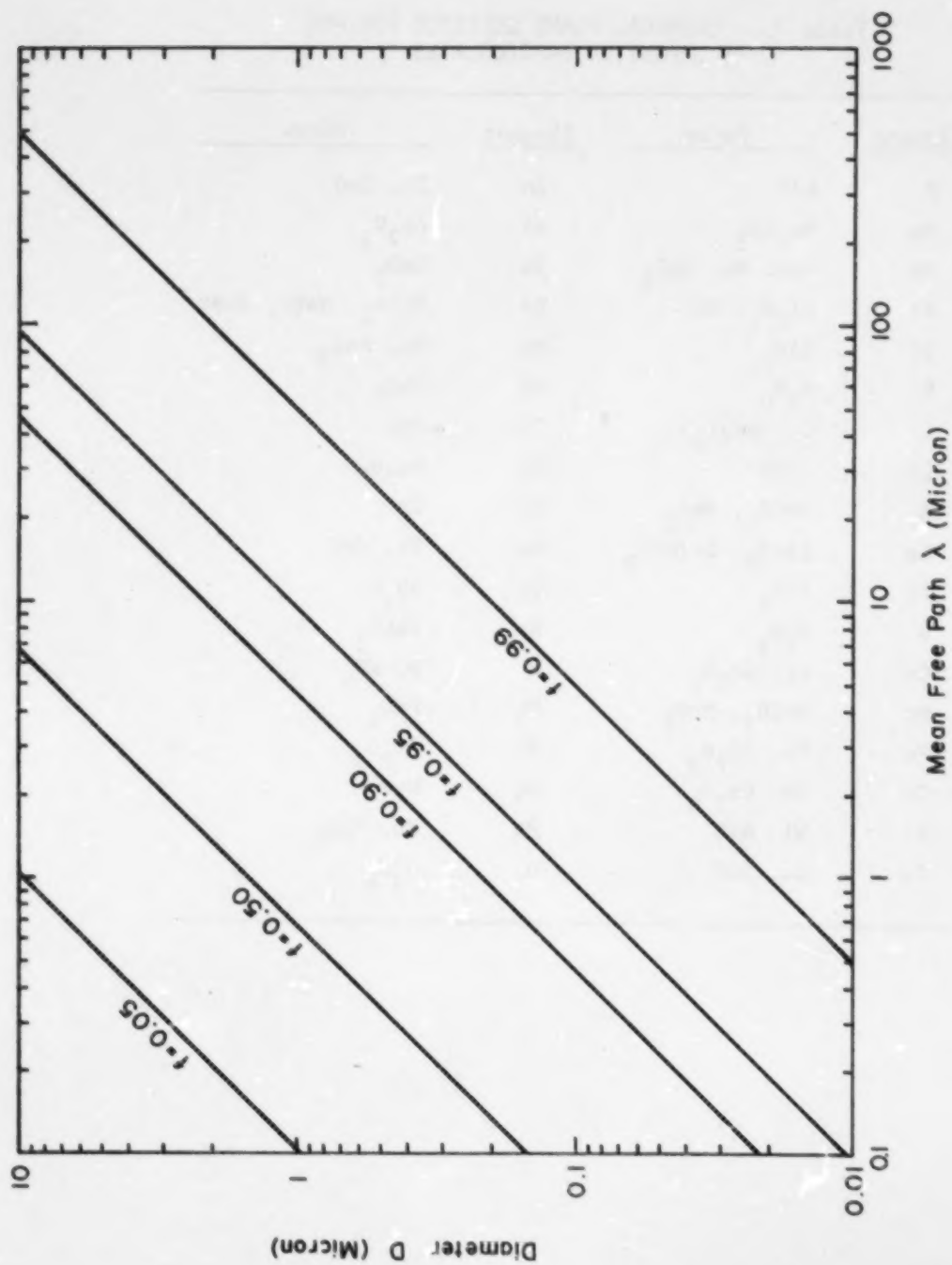


Figure 4. Probability of escape from a uniform spherical source as a function of diameter and mean-free-path

Table 7. CHEMICAL FORMS SELECTED FOR USE
AS DEPOSITED PARTICULATES

Element	Forms	Element	Forms
F	LiF	Zn	Zn, ZnO
Na	Na ₂ CO ₃	As	As ₂ O ₃
Mg	MgO, Mg, MgF ₂	Se	SeO ₂
Al	Al ₂ O ₃ , Al	Br	PbBr ₂ , NaBr, RbBr
Si	SiO ₂	Mo	Mo, MoO ₃
P	P ₃ N ₅	Rh	RhO ₂
S	S, (NH ₄) ₂ SO ₄	Pd	PdO
Cl	LiCl	Ag	Ag ₂ O
K	KHCO ₃ , KNO ₃	Cd	CdO
Ca	CaCO ₃ , Ca(OH) ₂	Sn	Sn, SnO
Ti	TiO ₂	Sb	Sb ₂ O ₃
V	V ₂ O ₅	Ba	BaCO ₃
Cr	Cr, Cr ₂ O ₃	W	W, WO ₃
Mn	MnCO ₃ , MnO ₂	Pt	PtO ₂
Fe	Fe, Fe ₂ O ₃	Au	Au ₂ O ₃
Co	Co, Co ₃ O ₄	Hg	HgO
Ni	Ni, NiO	Pb	Pb, PbO ₂
Cu	Cu, CuO	U	U ₃ O ₈

DESIRED DENSITY AND OTHER DATA FOR COMPOUNDS OF INTEREST

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APPENDIX A
SELF ABSORPTION IN A SPHERE

APPENDIX A

SELF ABSORPTION IN A SPHERE

The fraction of radiation escaping from a uniform spherical source in a specific direction can be obtained by direct integration of the attenuation equation. Figure 5 shows a volume element, with an attenuation path l , in a sphere with radius R . Using Σ for the macroscopic absorption cross section, the total radiation escaping from the disc element is for unit source strength.

$$\text{Total out from disc} = \int_{r=0}^{r=\sqrt{R^2-\chi^2}} 2\pi r e^{-\Sigma l} dr = 2\pi e^{\Sigma\chi} \int_{r=0}^{r=\sqrt{R^2-\chi^2}} r e^{-\Sigma\sqrt{R^2-r^2}} dr$$

After changing the integration variable to $y = \sqrt{R^2-r^2}$ and integrating by parts, one gets

$$\text{Total out from disc} = 2\pi e^{\Sigma\chi} \left[-\frac{R}{\Sigma} e^{-\Sigma R} + \frac{\chi}{\Sigma} e^{-\Sigma\chi} - \frac{1}{\Sigma^2} e^{-\Sigma R} + \frac{1}{\Sigma^2} e^{-\Sigma\chi} \right]$$

Integrating the disc contribution over the entire sphere and factoring the final form gives

$$\text{Total out from sphere} = \int_{\chi=-R}^{\chi=R} \text{Total out from disc} d\chi = \frac{4\pi R}{\Sigma^2} - \frac{2\pi}{\Sigma^3} (1-e^{-2\Sigma R})(1+\Sigma R)$$

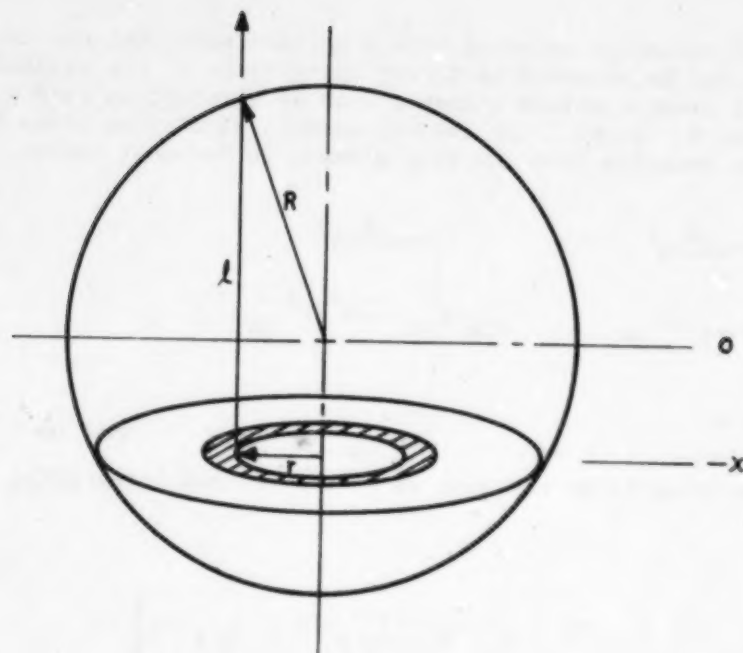


Figure 5. Geometry and notation used for describing escape of x-ray from within a spherical particle

For small values of Σ , this can be simplified as follows:

$$\begin{array}{l} \text{Total out for} \\ \text{small } \Sigma \end{array} = \frac{4}{3}\pi R^3 (1-2\Sigma R)$$

The fraction of radiation escaping compared to a non absorbing sphere is obtained by dividing either of the last two equations by $4\pi R^3/3$.

APPENDIX B
SERIAL NUMBER LISTS

IIT RESEARCH INSTITUTE

<u>Compound</u>	<u>Element Sought</u>	<u>Serial #</u>	<u>Weight (ug/cm²)</u>
<u>Co</u> ₃ O ₄	Co	001-1	0.755
		002-2	1.51
		003-5	3.78
		004-10	7.55
		005-50	37.8
		006-100	75.5
<u>Ti</u> O ₂	Ti	007-1	0.595
		008-2	1.19
		009-5	2.98
		010-10	5.95
		011-50	29.8
		012-100	59.5
<u>Zn</u> O	Zn	013-1	1.09
		014-2	2.18
		015-5	5.45
		016-10	10.9
		017-50	54.5
		018-100	109
<u>Ni</u> O	Ni	019-1	0.718
		020-2	1.44
		021-5	3.59
		022-10	7.18
		023-50	35.9
		024-100	71.8
<u>Pt</u> O ₂	Pt	031-1	1.65
		032-2	3.30
		033-5	8.25
		034-10	16.5
		035-50	82.5
		036-100	165

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<u>Compound</u>	<u>Element Sought</u>	<u>Serial #</u>	<u>Weight (ug/cm²)</u>
<u>CaF₂</u>	Ca	037-1	2.10
		038-2	4.20
		039-5	10.5
		040-10	21.0
		041-50	105
		042-100	210
<u>CaF₂</u>	F	037-1	1.75
		038-2	3.50
		039-5	8.75
		040-10	17.5
		041-50	87.5
		042-100	175
<u>MoO₃</u>	Mo	055-1	1.07
		056-2	2.14
		057-2	5.35
		058-10	10.7
		059-50	53.5
		060-100	107
<u>BaSO₄</u>	Ba	061-1	1.27
		062-2	2.54
		063-5	6.35
		064-10	12.7
		065-50	63.5
		066-100	127
<u>BaSO₄</u>	S	061-1	.296
		062-2	.592
		063-5	1.48
		064-10	2.96
		065-50	14.8
		066-100	29.6
<u>Al₂O₃</u>	Al	067-1	1.08
		068-2	2.16
		069-5	5.40
		070-10	10.8
		071-50	54.0
		072-100	108
<u>PdO</u>	Pd	073-1	2.47
		074-2	4.94
		075-5	12.4
		076-10	24.7
		077-50	124
		078-100	247

IITRI X-RAY FLUORESCENCE STANDARDS

Compound	Element Sought	Serial #	Weight ($\mu\text{g}/\text{cm}^2$)
<u>SiO₂</u>	Si	043-1	.879
		044-2	1.76
		045-5	4.40
		046-10	8.79
		047-50	44.0
		048-100	87.9
<u>CuO</u>	Cu	049-1	.386
		050-2	.772
		051-5	1.93
		052-10	3.86
		053-50	19.3
		054-100	38.6
<u>HgO</u>	Hg	079-1	.847
		080-2	1.69
		081-5	4.23
		082-10	8.47
		083-50	42.3
		084-100	84.7
<u>WO₃</u>	W	091-1	1.34
		092-2	2.69
		093-5	6.72
		094-10	13.4
		095-50	67.2
		096-100	134
<u>SnO₂</u>	Sn	097-1	.832
		098-2	1.66
		099-5	4.16
		100-10	8.32
		101-50	41.6
		102-100	83.2
<u>As₂O₃</u>	As	103-1	.765
		104-2	1.53
		105-5	3.82
		106-10	7.65
		107-50	38.2
		108-100	76.5

<u>Compound</u>	<u>Element Sought</u>	<u>Serial #</u>	<u>Weight ($\mu\text{g}/\text{cm}^2$)</u>
<u>NaCl</u>	Na	085-1	1.11
		086-2	2.22
		087-5	5.55
		088-10	11.1
		089-50	55.5
		090-100	111
<u>NaCl</u>	Cl	085-1	1.71
		086-2	3.43
		087-5	8.56
		088-10	17.1
		089-50	85.6
		090-100	171
<u>Ag</u>	Ag	109-1	5.5
		110-2	11.0
		111-5	27.4
		112-10	54.8
		113-50	274
		114-100	549